

## **Methods and Apparatus for the Oxidation of Glucose Molecules**

This application claims the benefit of U.S. Provisional Application No. 60/255,608 filed December 14, 2000.

### **Field of the Invention**

The present invention relates to the field of inorganic catalysts, and the use of such catalysts in the oxidation of organic molecules.

### **Background of the Invention**

Electrochemical oxidation of glucose has been studied for the potential applications as a detector for dissolved glucose in blood or other media. Current commercial blood glucose sensors use an enzyme electrode to oxidize glucose, which is followed with an indirect electrochemical detection of the enzymatic reaction products. Enzyme is relatively expensive, with a limited shelf-life, a low tolerance to elevated temperature, and it is not suitable for industrial applications. Glucose oxidase and glucose hydrogenase were the common enzymes to be immobilized in electrodes and to have selective reactions with glucose in a solution. Inorganic catalyst materials have the advantages of direct electrochemical oxidation, a longer shelf-life, and are resistant to the high temperatures and other harsh operating conditions found in a bioreactor or other industrial applications. The previous investigated materials of inorganic electrocatalysts include platinum, gold, ruthenium, iridium, their mixtures, and their oxides. A high oxidation potential was required to oxidize glucose and the current density was low, thus unfavorable for practical devices of glucose oxidation.

Although the theoretical concept of using glucose to power a bio-fuel cell has been mentioned in the past, a workable glucose-air fuel cell has not been demonstrated due to poor performance of the previously tested catalysts which include enzymes. The previous power densities reported were in the orders of microwatts per square centimeters. Glucose is inexpensive, safe, commonly available, conveniently stored, non-toxic, and hazard free. It offers certain advantages over the common fuels considered for portable fuel cells, such as hydrogen, methanol, and borohydride.

In US Patent 5,660,940, a biofuel-powered fuel cell is described with glucose, arabinose, and other carbohydrates as possible fuels. The fuel cell operates at above 90 °C with a two-step oxidation process using platinum, ruthenium, and vanadium as catalysts. In US Patent 5,976,719, a biofuel cell is described with glucose as a possible fuel. The oxidation is indirect and requires a microorganism to react with the glucose to generate other species to power the fuel cell. In US Patent 4,294,891, an implantable bio-oxidant fuel cell is described using glucose as a fuel and platinum, ruthenium, rubidium, iridium, nickel as catalysts for the anode. The power generated was in microwatts range. In US Patent 4,447,506, a ternary fuel cell catalyst containing platinum, cobalt, and chromium was disclosed for use as cathode material for oxygen reduction in acid medium, but not to be used as an anode.

### **Summary of the Invention**

This invention provides the composition of a catalyst that allows direct electrochemical oxidation of organic molecules, including carbohydrates and short chain alcohols. This invention further provides the composition of a catalyst that allows direct electrochemical oxidation of dissolved glucose in neutral and alkaline media, with a very low oxidation potential and moderate to high current density. The methods of preparing this catalyst into a working electrode are described by examples. The application of this invention is demonstrated by a room temperature direct glucose-air fuel cell having an open circuit voltage of 1.08 V and a peak power density of 3 mW/cm<sup>2</sup>. Other organic molecule based fuels like arabinose, mannitol, galactose, mannose, sorbitol, xylose, methanol, and ethanol can also power the fuel cell with different power densities. In another example, the application of this invention for detecting dissolved glucose under physiological conditions is also shown.

### **Brief Description of the Drawings**

FIG. 1(a) is a cyclic voltammogram of a Pt wire electrode in 0.016 molar glucose in a pH 7.4 buffer solution;

FIG. 1(b) is a cyclic voltammogram of a Pt/Co/Co<sub>3</sub>O<sub>4</sub> deposited wire electrode in 0.016 molar glucose in a pH 7.4 buffer solution;

FIG. 2 is a schematic representation of a Pt-wire electrode with a layered catalyst;

5 FIG. 3 is a schematic representation of a flow injection analysis cell;

FIG. 4 is a graph showing the oxidation current transient response to glucose injection in a flow injection analysis;

10 FIG. 5 is a graph showing the peak current in FIA versus glucose concentration;

FIG. 6 is a graph showing an in-situ FTIR for 0.15 M glucose oxidation on Pt/Co/Co<sub>3</sub>O<sub>4</sub> in a pH 7.4 phosphate buffer;

15 FIG. 7 is a graph showing the anode performance during oxidation of 0.5 M glucose in 0.5 M NaOH at 20°C;

FIG. 8 is a scanning electron micrograph of a Pt/Co/C electrode surface;

20 FIG. 9 is a schematic diagram of an exploded view of a test fuel cell;

FIG. 10 is a graph showing the discharge characteristics of a room temperature direct glucose-air fuel cell;

25 FIG. 11 is a schematic diagram showing the components in the structure of an anode including a hypothetical view of a microstructure containing PTFE;

FIG. 12 is a schematic diagram showing the components in the structure of an anode including a hypothetical view of a microstructure containing no PTFE;

30 FIG. 13 is a graph showing the performance of an Pt/Co/C anode prepared by chemical reduction; and

35 FIG. 14 is a graph showing a comparison of the constant current oxidation of different sugars and compounds on a Pt/Co anode.

### **Detailed Embodiment of the Invention**

40 This invention discloses a combination of electrode materials that can electrochemically oxidize organic molecules. This invention further discloses a combination of electrode materials that can electrochemically oxidize glucose at a very low potential and with a high current density. The low oxidation potential of glucose allows the development of an inorganic glucose sensor with  
45 minimum interferences from other dissolved constituents. The use of an inorganic electrocatalysts as described in this invention will not have the disadvantages noted above for current commercial

5 blood glucose sensors. The use of such an electrocatalyst for detecting dissolved glucose in neutral buffer can be demonstrated.

10 The effectiveness of the present invention can be demonstrated by using a small direct glucose-air alkaline fuel cell with a single cell open circuit voltage (OCV) of 1.08 V and a power density of 3 mA/cm<sup>2</sup>, operating at room temperature. At room temperature, this OCV exceeds those practically achieved for a methanol-air fuel cell, the primary contender for commercial small scale fuel cells. With the application of the electrocatalyst in this invention, the use of glucose as a power source for portable consumer electronics devices is possible. The use of glucose as a fuel has many advantages when compared to such fuels as hydrogen, methanol, and borohydride. Glucose is  
15 inexpensive, commonly available, conveniently stored, safe, non-toxic, and hazard free. The theoretical energy per volume for glucose is the highest if compared to methanol and hydrogen and has a good potential for micro or small scale fuel cells.

20 The use of precious metals such as platinum, gold, ruthenium, rhodium, iridium, and their alloys and oxides as electrocatalysts for electrochemical oxidation of glucose has generally been reported for acidic, neutral, and alkaline media. The motivation of previous studies was to develop an electrode for electrochemical detection of glucose. A glucose-air fuel cell had not been conceived to be practical. The problems of these electrocatalysts, as listed in TABLE 1, is their high oxidation potentials and low current densities, in other words, the low catalytic activity of the  
25 metals and their combination for electrooxidation of glucose.

This invention discloses that by adding cobalt or its oxides to platinum, the activity for glucose oxidation can be markedly increased in alkaline and neutral media. As shown also in TABLE 1, the oxidation potential is as low as -0.8 V /Hg/HgO with an oxidation current of 5  
30 mA/cm<sup>2</sup> in the alkaline medium. This provides the possibility of a room temperature direct glucose-air fuel cell which in the past had not been demonstrated. The role of cobalt is related to its multiple oxidation states and its bi-functional character of oxidizing intermediates like carbon monoxide and carbonyl function groups.

5 The comparison of the glucose-air fuel cells and other glucose-oxygen fuel cells reported in the literature are shown in TABLE 2. Most of the reported data are intended for implantable and biofuel cell applications. The power densities obtained using platinum black or enzyme electrodes were only in microwatts per sq. cm as opposed to the 3 mW / cm<sup>2</sup> value obtained in this invention.

10 The increase in activity of the PtCo alloy can be demonstrated by comparing the cyclic voltammograms of glucose on a platinum electrode and a platinum/cobalt/cobalt oxide electrode in a phosphate buffer, as is shown in Figures 1(a) and 1(b). In Figure 1(a), the cyclic voltammogram is shown for a Pt wire electrode in phosphate buffer (pH 7.4) at 10 mVsec<sup>-1</sup> in a solution with 0.016 M glucose and without glucose. As seen in Fig. 1(a), a low activity for platinum is shown for glucose oxidation. In Figure 1(b), the cyclic voltammogram is shown for a Pt/Co/Co<sub>3</sub>O<sub>4</sub> deposited wire electrode in phosphate buffer (pH 7.4) at 10 mV sec<sup>-1</sup> in a solution with 0.016 M glucose and without glucose. A schematic representation of such an electrode is shown in Figure. 2. As seen in Figure. 1(b), a twenty times increase in the peak current density is observed at a potential of -0.4 V /SCE for the oxidation of glucose on Pt/Co/Co<sub>3</sub>O<sub>4</sub> in a neutral buffer solution.

15 The applicability of such an electrocatalyst as a glucose sensor is demonstrated in a flow injection analysis setup like the one shown in the schematic diagram in Figure 3. The applied oxidation potential is 0.250 V vs Ag/AgCl. Figure 4 shows the oxidant current transient response to glucose injection in a flow injection analysis experiment. The sensitivity and repeatability of the oxidation peak current is demonstrated in Figure 4 by the series of oxidation current peaks in response to corresponding injections of dissolved glucose of different concentrations. A platinum wire with platinum, cobalt and cobalt oxides deposited was used as the sensing electrode. In Figure 5, the corresponding dynamic linear response range for the glucose concentration is shown. Figure 5 shows the peak current in FIA versus glucose concentration.

20 The intermediate products of direct glucose oxidation with Pt/Co/Co<sub>3</sub>O<sub>4</sub> in a pH 7.4 phosphate buffer were identified by in-situ Fourier transform infra red spectroscopy (FTIR). Figure 6 shows an in-situ FTIR-RAS for 0.15 M glucose oxidation on Pt/Co/Co<sub>3</sub>O<sub>4</sub> in a pH 7.4 phosphate buffer. As shown in Figure 6, the product clearly identified was carbon dioxide 2342 cm<sup>-1</sup> and an intermediate product gluconolactone at 1744 cm<sup>-1</sup> was also detected.

For fuel cell applications, the steady-state direct electrochemical oxidation of glucose on high surface area electrodes is demonstrated by chronopotentiometry as shown in Figure 7. The glucose solution is 0.5 molar in a 0.5 molar NaOH solution and the temperature is 20°C . The 0.283 cm<sup>2</sup> anode electrode for the half-cell studies is a carbon electrode deposited with platinum and cobalt. Figure 8 shows the scanning electron micrograph of a Pt/Co/C electrode surface. The scan electron micrograph of the surface of the electrode and corresponding energy dispersive x-ray (EDX) analyses showed 14.5 % atom cobalt and 85 % atom platinum. The applicability to a direct glucose-air fuel cell can be inferred from the results in Figure 7 and the well documented air cathode half-cell performance data.

The applicability of this invention to a room temperature direct glucose-air fuel cell is now demonstrated. A schematic representation of such a fuel cell is shown in Figure 9. An anode is prepared in the conventional method by mixing a high surface area carbon such as Vulcan 72, acetylene black with a 2 mg/cm<sup>2</sup> loading of Pt and a 1:1 atomic ratio of platinum to cobalt. The cobalt can be applied by electrochemical deposition or codeposition together with platinum from a dissolved chloride salt. The oxides of cobalt are also expected to be present. The cathode used can be a commercially available air cathode, such as Alupower AC65 air cathode with a silver catalyst. Using a 1.0 molar glucose solution in 1.0 molar NaOH, the open circuit voltage of such a glucose-air fuel cell can reach 0.95 V at 22 °C. No forced convection of the liquid or air was applied. The current density is 5 mA/cm<sup>2</sup> at a cell voltage of 0.4 V at room temperature. A 4 cm x 4 cm single cell using a 30 ml volume of the glucose/NaOH solution can turn a small motor fan for 3 hours giving a power density of 0.02 W/g of glucose and 0.05 Whr/g of glucose. Using a more concentrated 7M hydroxide solution, the peak power density improves to 3 mW cm<sup>-2</sup> or 0.035 W/g of glucose. The discharge of such a fuel cell in 7M KOH solution is shown in Figure 10. Using a platinum air cathode instead of the AC65 air cathode, the open circuit voltage can reach 1.08 V and power density can increase further. Performance of a room temperature direct glucose-air fuel cell at such a level has never been reported in the literature.

The performance of such a glucose-air fuel cell compares with open literature for conventional methanol-air fuel cells operating at room temperature. Direct methanol-air fuel cells

5 normally uses Pt/Ru as the electrocatalyst and operate above 60°C. A recent report states 20mW  
cm<sup>-2</sup> peak power density at 70°C in a methanol fuel cell with a pure oxygen flow to the cathode  
(Amphlett, J. C. et al., 2001, J. Power Sources, 96:204). Normally, an electric heater for preheating  
the electrolyte is needed for the methanol-air fuel cell. The theoretical open circuit voltage of  
methanol-air cell is 1.21 V compared to 1.23 V for glucose-air. A 1.08 V open circuit voltage is  
10 observed in the room temperature glucose-air cell using the electrocatalyst of this invention but an  
open circuit voltage below 0.8 is normally reported for the methanol-air fuel cell even at elevated  
temperatures (Amphlett, J.C. et al., 2001, J. Power Sources, 96:204).

15 The theoretical energy density of methanol in a methanol-air cell is 17.37 kJ/cm<sup>3</sup> but that for  
glucose is 24.57 kJ/cm<sup>3</sup> in a glucose-air cell. Theoretically, the number of electrons for complete  
electrooxidation of methanol is 6 but for complete oxidation of glucose is 24. In-situ FTIR  
experiments have detected the strong presence of glucono-lactone and carbon dioxide in the  
products of electrochemical oxidation of glucose in alkaline and neutral media at relatively low  
oxidation potentials, as shown in Figure 6. This demonstrates the effectiveness and intrinsic  
20 activity of the electrocatalyst of this invention, although there is room for improvement in the mass-  
transfer aspect of the electrode design.

25 The dissolved glucose cross-over effect has been determined to be a 50 to 100 mV lowering  
of the cathode potential depending on the current density. The activity of platinum-cobalt-oxide  
electrocatalyst for glucose oxidation is more than an order of magnitude above common catalysts  
including platinum. This cross-over effect can be minimized with a suitable choice of anionic  
conducting membrane.

30 The amount of cobalt in the catalyst composition is within the range of about 5 to 70 atom  
percent of the composition with the balance being Pt. If the amount of Co in the catalyst  
composition is to be expressed as a weight percent, then the Co is about 1.5 to about 48 weight  
percent of the catalyst composition. Likewise, if the amount of Co is to be expressed as an atom  
ratio, then the Co:Pt atom ratio is within the range of about 1:20 to 3:1. In another embodiment of  
the invention, the catalyst composition can include tin in addition to platinum and cobalt. If the  
35 composition includes tin, then the Co will be in the composition in an amount within the above

5 specified range with the balance of the catalyst composition being a mixture of platinum and tin. The oxidation state of the cobalt in the catalyst composition includes 0, 2, 8/3 or 3, although any oxidation state that provides a catalyst capable of oxidizing glucose may be used. The catalyst composition can be added to electrode forming materials to create a composite electrode or the catalyst composition can be supported on various support structures such as a metal wire (shown  
10 schematically in Figure 2), metal electrode, metal foam (shown schematically in Figures 11, 12), graphite electrode, a porous carbon electrode or a gas diffusion electrode.

In another embodiment, the electrocatalyst of the invention can be used to synthesize gluconic acid from a glucose solution. Gluconic acid is produced as a product during the oxidation  
15 of glucose. The electrocatalyst can therefore be employed to catalyze the oxidation of glucose to gluconic acid and the gluconic acid can be recovered from the solution.

The electrocatalyst in this invention can be prepared by several methods including impregnation, gas phase or solution phase chemical reduction, electrodeposition, vapour deposition,  
20 and electrochemical reactive deposition. The complete mixing of the different metals to form an alloy is not necessary to prepare the catalyst of the present invention. For example, the Co can be layered onto a supporting structure such as a Pt wire electrode like the one shown in Fig. 2. The Co can be added as an outside layer or the Co can be added side-by-side with Pt onto a wire electrode. Likewise, the Co can be added as an outside layer or side-by-side to an existing Pt and carbon  
25 structure. Some examples are described below.

### Example 1

A wire electrode with the electrocatalyst Pt/Co/Co<sub>3</sub>O<sub>4</sub> giving the results shown in Figure  
30 1(b) was prepared as follows. Platinum and cobalt were co-deposited on a platinum wire of 0.5 mm diameter from a mixed solution of 0.3 molar CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.032 molar chloroplatinic acid in deionized water (see Figure 2 for schematic diagram of layered wire electrode). The immersed depth of the working electrode was 1 cm. A three-electrode cell was used with a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Oxygen  
35 bubbles were introduced from a cylinder to impinge on the wire electrode so that reactive deposition



5 forming cobalt oxides of  $\text{CoO}(\text{OH})$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Co}_2\text{O}_3$  occurred. The details of reactive deposition to produce oxides of cobalt with high surface area are described in the literature (Jiang, S.P. et al, 1990, Electrochem. Soc. 137:3374). The deposition was controlled galvanostatically at  $17 \text{ mA/cm}^2$  for 300 seconds and the rate of bubbling oxygen was about 3 ml/min. Under this preparation, most of the cobalt oxides formed are in the form of  $\text{Co}_3\text{O}_4$  with an oxidation state of 8/3.

### Example 2

10 An anode carrying the electrocatalyst of this invention is prepared from a carbon electrode (ELAT electrodes from E-TEK Corp, New Jersey) by electrodeposition in a 0.04 molar  $\text{H}_2\text{PtCl}_6$  and 0.098 molar  $\text{CoCl}_2$  solution at  $50 \text{ mA cm}^{-2}$  for 30 minutes. The resulting surface is analyzed to have 15 85.1 atom% Pt, 14.6 atom% Co and 0.3atom% Cl by EDX analyses. X-ray photoelectron spectroscopy indicated the oxidation state of cobalt is zero. The surface morphology is shown in Figure 6 with appreciable roughness. The performance of this anode for the oxidation of 0.5 molar glucose in 0.5 molar NaOH is shown in Figure 7.

### Example 3

20 An anode carrying the electrocatalyst of this invention is prepared by a chemical reduction method. Vulcan 72 activated carbon was added to a solution containing 40 mM hexachloroplatinic acid and 120 mM cobalt acetate in a ratio of 1 g to 50 ml. Excess hydrazine was added to reduce the platinum and cobalt. The carbon is used to make a paste with acetylene black and 60% 25 polytetrafluoroethylene (PTFE) aqueous emulsion in the ratio of 70%, 10%, and 20% by weight respectively. The paste is applied to a piece of 1.5 mm thick,  $400 \text{ g m}^{-2}$  nickel foam. Figure 13 shows the performance of a Pt/Co/C anode prepared by chemical reduction. The electrochemical oxidation of 0.5 molar glucose oxidation in 0.5 molar NaOH at  $5 \text{ mA cm}^{-2}$  is shown in Figure 13 (i.e., the anodic oxidation is 0.5 M glucose in 0.5 M NaOH at  $5 \text{ mA cm}^{-2}$  at  $20^\circ\text{C}$ ).

### Example 4

30 A glucose fuel cell anode carrying the electrocatalyst of this invention is prepared with a common method of making a porous electrode as follows. An activated carbon with 10% Pt loading from Heraeus Co. was the source of the Pt. The Pt particles have a narrow size distribution 35 of 1.5 to 3.0 nm. Six grams of this powder was mixed uniformly with 0.224 g of acetylene black

5 and 1.2 g aqueous emulsion of PTFE (60% by weight) and ethanol with continuous stirring to make  
a paste. 0.38 gram of the paste was then applied to a 4 cm x 7 cm 400g m<sup>-2</sup> nickel foam which  
serves as the current collector (nickel mesh could also be used as the current collector). A small  
amount of cobalt was electrochemically deposited to the electrode. A 10:90 dried weight ratio of  
PTFE to catalyst was used in this example (Alternatively, the PTFE could be replaced by a  
10 hydrophilic ("wetting") binder, or not be present at all). The electrode is a "flooded" electrode  
without the presence of gas or a gas-liquid interface. The electrode is completely immersed in the  
liquid fuel and electrolyte solution. The performance of such an anode is demonstrated in a  
glucose-air fuel cell using two Alupower AC-65 air breathing cathodes of either side of the anode.  
The total surface area is therefore 56 cm<sup>2</sup>. The fuel is 6 ml of a 1.85 molar glucose in 7 molar  
15 KOH. The discharge behavior at a current of 200mA of the cell at 20°C is shown in Figure 10. The  
starting power is above 3 mW cm<sup>-2</sup> and the average power density in the first 20 minutes is 2.5mW  
cm<sup>-2</sup>. Using a 0.6 mg cm<sup>-2</sup> platinum loading cathode and an anionic membrane, the open circuit  
voltage can reach above 1.08 V at room temperature.

### 20 Example 5

Figure 14 shows a comparison of the constant current oxidation of different sugars and  
compounds on a Pt/Co anode. The electrochemical oxidation of other carbohydrates and related  
compounds is demonstrated with an anode prepared as follows. A platinum disk as a cathode is  
immersed in a solution of 0.045 molar H<sub>2</sub>PtCl<sub>6</sub> and 1 molar CoCl<sub>2</sub> solution and a deposition current  
25 of 2.5 mA cm<sup>-2</sup> was passed for 30 minutes. The electrode is then used as an anode for half cell  
studies of oxidation of various sugars and compounds in 0.5 M NaOH. The resulting  
chronopotentiograms are shown in Figure 14.

Although preferred embodiments of the invention have been shown and described, it should  
30 be understood that various modifications and substitutions, as well as rearrangements and  
combinations, can be made by those skilled in the art, without departing from the spirit and scope of  
this invention.

**TABLE 1.** Comparison of electrocatalysts for glucose oxidation.

<u>Reference</u>	<u>Electrocatalyst</u>	<u>Electrolyte</u>	<u>Oxidation Potential</u>	<u>Current Density</u>
Neuburger & Johnson[1]	gold	0.2 M NaOH	0.4V Ag AgCl	0.02 mA/cm <sup>2</sup>
Bae et al.[2]	platinum	0.1 M HClO <sub>4</sub>	0.0 V/SCE	0.05 mA/cm <sup>2</sup>
Vassilyev et al.[3]	rhodium	PH 7.2 buffer	0.6 V RHE	0.01 mA/cm <sup>2</sup>
Vassilyev et al.[3]	iridium	PH 7.2 buffer	0.4 V RHE	0.02 mA/cm <sup>2</sup>
Prabhu and Baldwin[4]	Copper CME	0.15M NaOH	0.4 V Ag AgCl	0.4 mA/cm <sup>2</sup>
Wang and Taha [5]	RuO <sub>2</sub>	1 M NaOH	0.4V Ag AgCl	0.2 mA/cm <sup>2</sup>
Reim and Van Effen [6]	Nicket(III) Oxide	0.15M NaOH	0.45V Ag AgCl	0.2 $\mu$ A/cm <sup>2</sup>
Santos and Baldwin [7]	CoPC	0.15M NaOH	0.4 V Ag AgCl	0.5 $\mu$ A/cm <sup>2</sup>
Zhou and Wang [8]	Prussian Blue CME	0.5M KCl	0.4V SCE	0.2 $\mu$ A/cm <sup>2</sup>
Zhang et al. [9,10]	Pt WO <sub>3</sub>	0.5M H <sub>2</sub> SO <sub>4</sub>	0.0 V/SCE	6 mA/cm <sup>2</sup>
This invention	Pt Co O C	0.5M NaOH	-0.80 V/Hg/HgO	5 mA/cm <sup>2</sup>

**TABLE 2.** Comparison of glucose-air or glucose-oxygen fuel cells.

<u>Reference</u>	<u>Electrocatalyst</u>	<u>Electrolyte</u>	<u>Power Density</u>	<u>Temperature</u>
Wan and Tseung [11]	Platinum black	0.5 M NaCl	20 $\mu$ W/cm <sup>2</sup> 3.3 $\mu$ W/ (in vivo)	37 °C
Chen et al. [12]	Glucose oxidate and Osmium complex	Citrate buffer pH 5	64 $\mu$ W/cm <sup>2</sup> 137 $\mu$ W/cm <sup>2</sup>	23 °C 37 °C
This invention	Pt Co O C	7 M KOH	3 mW/cm <sup>2</sup>	20 °C

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